

UNITED STATES ENVIRONMENTAL PROTECTION AGENC.

REGION I

J.F. KENNEDY FEDERAL BUILDING, BOSTON, MASSACHUSETTS 02203-2211

August 12, 1993

Todd Bobar, RPM U.S. Department of the Navy Northern Division 10 Industrial Highway Code 1823 - Mail Stop 82 Lester, PA 19113-2090



Dear Mr. Bobar:

Attached you will find EPA's comments on the proposed workplan from Battelle Ocean Sciences and the draft ecological marine assessment workplan from Menzie Cura and Associates, both dated July 19, 1993. These proposed workplans were designed to help measure the impacts to the marine environment of Narragansett Bay due to the operations of the Naval Education and Training Center (NETC).

As you are aware, many issues were raised, discussed and resolved at the meeting of July 28th at NETC. I would to take this opportunity to present a brief summary of the more significant discussions. It was agreed that the proposed sampling depths for each of the near-shore sediment sampling locations would be revised from 0-4 cm and 20-24 cm to a composite sample collected from 0-15 cm. This depth was selected as the depth of sediments available to the benthic community due to bioturbation. Therefore, the number of analyses per boring was reduced from two (2) samples per boring to one (1).

In response to this reduction in the number of analyses per boring, it was agreed that the Navy would collect three to four additional near-shore sediment samples along McAllister Point from areas closer to Coddington Cove, which is a likely depositional environment for sediments. In addition, the Navy agreed to install a series of piezometers/micro wells along the near-shore edge of McAllister Point landfill. This additional effort would provide valuable insight into the rate, direction and classification (i.e., fresh water vs. salt water) of the groundwater flow in the area(s) between McAllister Point landfill and the adjacent bay sediments. These piezometers/micro wells should be designed to also provide representative groundwater samples for analyzing the concentrations of contaminants within the groundwater.

We had also agreed to move the background reference locations to areas which are more likely to be free of anthropogenic activity. Location-specific information from the State representatives provided valuable insight into the selection of these new locations. I believe these new locations were accurately described at the meeting.

Attached you will find a copy of EPA comments and recommendations. These comments and recommendations have been listed as both general and specific in nature and have been numbered for future reference. If there are any questions with either the summary of the July 28th meeting at NETC or the attached comments, please feel free to call me at 617/573-9614.

Sincerely,

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Andrew F. Miniuks, Remedial Project Manager Federal Facilities Superfund Section

Attachment

CC: Paul Kulpa, RI DEM
Greg Fine, RI DEM
Mary Sanderson, EPA
Susan Svirsky, EPA
Ken Finkelstein, NOAA
Mike Kulbersh, CDM-FPC

ATTACHMENT I

General Comments

1. The sediment toxicity test must be performed at the same time and location as the sediment chemistry analyses and the in-situ measures of biological conditions. If the Navy at this time chooses not to perform the sediment toxicity testing, and EPA determines that sediment toxicity testing is required at the sites under investigation, then each aspect of the sediment triad will have to be resampled and retested. This information must all be collected simultaneously.

The sediment triad method combines sediment toxicity test measures, sediment chemistry analyses, and in-situ measures of biological conditions (the latter two already planned for completion by Battelle and Menzie-Cura) as a means of quantitatively assessing pollution-induced degradation of the benthic environment. The rational for this method is that each component provided information complementary to the other two and that together all three components provide sensitive, balanced and objective approach to determining pollution effects on living resources. Sediment toxicity can be measured using one or both of two standard methods: the solid-phase acute toxicity test with the marine amphipod Ampelisca abdita and the early-life stage toxicity test with the sea urchin Arbacia punctulata modified for exposures to sediment pore-water samples.

- Since accurate positional information will be collected for this phase of the sediment and biota sampling effort, the positional data should be maintained pending EPA review of the analytical data. If warranted, these sampling areas could be revisited to collect additional sediment for the toxicity testing.
- 3. There is concern over the sequence of events in this sediment and biota characterization effort. As currently proposed, the benthic survey will follow the sediment/biota collection. It is likely that the areas to be sampled will be greatly disturbed during the first effort, potentially altering the species composition of the subsequent sample significantly.

Revise the workplan to ensure that the benthic survey is completed prior to collecting the sediment/biota samples.

4. The workplan does not describe the methodology to be followed if both mussels and clams are not found concurrently at all locations due to their differing habitat preferences. Both species are necessary components of this sampling event.

Revise the workplan to describe the procedures and supporting rationale for this scenario.

- 5. Revise the workplan to ensure that the specimens of mussels collected during this sampling effort are at a size of greater than 8 cm and clams greater than 6 cm. These samples would have a greater potential for bioaccumulating contaminants and being more representative of an edible size class. Ensure that the minimum size of the collected clam and mussels samples comply with the legal size limit within the State of Rhode Island.
- 6. Revise the workplan to ensure that the near-shore sediment samples are not composited. If fifteen sampling stations are necessary to characterize the near-shore sediment chemistry of McAllister Point landfill, then fifteen individual samples should be collected.
- 7. Revise the workplan to ensure that all samples collected for inorganic analyses are <u>not</u> packaged in aluminum foil.

 Organic samples may be packaged in foil, after a hexane rinse and deionized water (DI) rinse. The Navy may want to consider a simpler approach which is to use wide mouth ICHEM jars with teflon cap liners, which are suitable for either suite. This revision to the workplan must ensure that the samples will be stored at a <u>minimum</u> of -20 C.
- 8. The performance of field and laboratory activities described in the proposed workplan from Battelle is based almost entirely on Battelle Standard Operating Procedures (SOPs). The text frequently refers to these SOPs which are not among the documents submitted for review.

Include in the response to these comments, all of the SOPs referenced in the Battelle workplan. Of particular interest are SOPs 5-128, 5-157, 5-190, 5-192, 5-196, and MSL-M-33. These specific SOPs address procedures for the analyses of PCBs, PAHs, metals, and Butyltins in tissue and in sediments.

9. Since the quantitation limits specified for the analytical parameters are extremely low, a copy of Battelle's most recent method detection limit (MDL) study must be appended to the plan. The MDL study must clearly indicate the laboratory's ability to quantify and identify all the analytes of concern at the quantitation limits specified.

Revise the workplan accordingly.

10. The specific use of the analytical data is not provided in the Battelle workplan. The data will help determine the extent and nature of the contamination, the Navy should produce an ecological risk assessment.

If the ecological risk assessment is developed via the proposed workplan from Menzie-Cura and Associates, then this information should be included in the Battelle Workplan. Conversely, the proposed workplan from Menzie-Cura and Associates should reference the source of the data to be used in the development of the ecological risk assessment.

- 11. Include in this revision a discussion of the chemical levels of concern and an explanation for the AVS/SEM analyses and the TOC and grain size analyses.
- 12. Revise the Battelle workplan to ensure consistency between the off-shore sample numbers presented in Table 2 and Figure 1-3.
- 13. Revise the proposed workplan to include a discussion of collecting sediment samples from depositional locales. This issue was raised in the meeting on July 28, 1993.
- 14. Revise the proposed workplan from Menzie-Cura and Associates to ensure that the redox potential is determined by a portable Eh meter rather than relying on observing the depth of the surface oxidized layer.

Specific Comments - Battelle

Page 6, Section 2.0, Technical Approach.

15. The text states that in all, a total of 55 sediment cores, 31 mussel samples, and 31 clam samples will be collected. In following the proposed compositing scheme described in the text, the total number of sediment cores also appears to be 31. Revise the workplan to resolve this apparent inconsistency.

As previously mentioned, the near-shore sediment samples should not be composited. Ensure that the revised workplan clearly describes the derivation of the total number of core samples.

16. Revise the workplan to ensure that field duplicates are taken at every 1 of 5 off-shore sampling locations and at one background location.

Page 10, Sediment Sample Collection.

17. The text states that sediment samples will be collected with polybutyrate cores. Since these cores may contribute to phthalate contamination of the sediment sample, the text needs to consider this possibility in the selection of the core liner.

The Navy should consider using stainless steel core liners for this purpose.

- 18. The text states on page 14 that, for the intertidal sampling stations, the core liner will be driven into the sediment.

 Revise the workplan to include a description of the procedure for driving the core liners.
- 19. The text states on page 14 that the overlying water will be siphoned off the top of the sediment using a pre-cleaned tygon tubing. Tygon may cause phthalate contamination which could interfere with the PCB analysis. Therefore, the tygon tubing must not contact the sediment and Teflon tubing should be used for siphoning the overlying water.

Revise the workplan to ensure that the tygon tubing will not contact the collected sediment samples or use Teflon tubing for siphoning the overlying water.

Page 15, Bivalve Sample Collection.

20. The text states that bivalves will be removed by hand with the use of polyethylene or other non-contaminating gloves. Poly- ethylene gloves are not recommended for collecting the bivalve samples, rather nitrile gloves are preferred so as to reduce the potential phthalate contamination.

Revise the workplan to include the use of nitrile gloves for removing/collecting the bivalves.

21. The text states that all bivalve samples will be double wrapped in aluminum foil. Bivalves collected for metals determination must not be wrapped in aluminum foil due to the potential for interference from the aluminum. These samples must be double wrapped in plastic bags or consider using wide- mouth ICHEM jars with teflon cap liners.

Page 16, Field Quality Control Samples.

22. The text states that the sediment field duplicate should be collected within 5 m of the original core. A sediment field duplicate must be co-located; a field duplicate sample collected 5 m from the original sediment field sample is too far to be considered a duplicate sample.

Revise the workplan accordingly.

Page 24, Section 2.2, Laboratory Analytical Methods.

23. The text indicates that the analysis for Total Organic Carbon (TOC) will be performed. The analyses for TOC in sediments should follow the attached Special Analytical Services method (see Attachment 2).

Page 25, Table 5, Number and Types of Samples to Be Analyzed in the Laboratory.

- 24. Since the explanation for indicating that only 31 tissue samples for Butyltin analysis will be made is given later in the text in Section 2.2.2, on page 35, a footnote to Table 5 needs to be given to reference this explanation.
- 25. Page 36, Section 2.2.3.2, Trace Metal Instrumental Analysis.

The text states that the analysis for mercury will be performed using modifications of EPA Method 245.5 for sediments and 245.6 for tissue and that modified EPA Method 200.8 will be used for all other metals (except selenium, iron, calcium, and chromium).

Since the Detection Limits for these EPA methods are not as low as those listed in Table 6, revise the text to acknowledge these differences and describe the modifications that will be made to the EPA methods to meet the lower Detection Limits.

26. Since EPA Method 200.8 is inappropriate for the determination of boron, magnesium, potassium, and sodium, the text needs to indicate or explain how the modified Method 200.8 will enable these analyses to be completed.

- 27. Revise the workplan to clearly identify the proposed analytical methods for determining the presence and concentrations of selenium, iron, calcium, and chromium.
- Page 37, Section 2.2.5, TOC and Grain Size Analysis.
- 28. The text states that the Grain Size analysis will be performed by the standard sieve-pipette method. Revise the text to clearly identify or reference the appropriate method for this determination.
- Page 38, Section 3.1.1, Sample Quality Control.
- 29. The text states, for Butyltin Analysis, that one procedural blank and one matrix spike will be processed with each batch of samples. Revise the text to clearly state that Butyltin analysis needs to include a laboratory duplicate with each batch of 20 samples.
- Page 40, Section 3.1.3, Validation.
- 30. The text provides no specific procedures for data validation. The text needs to state that validation will follow the Region I Laboratory Data Validation Functional Guidelines For Evaluating Organic Analyses; 2/1/88; modified 11/1/88; and Region I Laboratory Data Validation Functional Guidelines For Evaluating Inorganics Analyses; 6/13/88; modified 2/89.

Specific Comments - Menzie-Cura and Associates

Page 1, Introduction.

- 31. Revise the workplan to include the rationale for the locations for assessing the marine benthic infauna and epifauna, or cite the report which provides the rationale for the selection.
- Page 2, Field Sampling: Benthic Infauna
- 32. Describe the sediment characteristics that will be assessed and the type of equipment that will be used to make these sediment measurements. If appropriate, reference the report which provides this information.

33. Describe whether or not Menzie-Cura and Associates will be using the same field logs as provided in Battelle's proposed workplan. If not, then provide a sample of a field recording log that will be used during the sampling program. Suggested items that should be recorded during the sampling event include: longitude/latitude, approximate depth of water (fathoms), water and air temperature, salinity, redox potential of collected sediment, high or low tide.

Photographs should be taken of the collected benthos during the field sampling aboard the vessel as part of the benthos characterization.

Page 3, Field Sampling: Benthic Infauna

- 34. The fourth sentence of the third paragraph should state "Numerical" predominant species will be identified.
- 35. Describe the previous studies of the Narragansett Bay that provide the taxonomic analyses results that are to be used for comparison with the results of this assessment. Why are these studies appropriate for comparison?
- 36. Describe the standard marine benthic assessment protocol developed by the EPA EMAP program that will be used for this benthic assessment. Either provide detail of the EMAP protocol or cite the document which describes the EMAP marine benthic assessment protocol.

Page 3, Field Sampling: Epifauna

- 37. Describe whether or not the term "composition" in the third sentence refer to taxonomic and numerical composition. If yes, then describe the procedure for determining the numerical evaluation.
- 38. Describe the purpose for the photographs that will be obtained of the representative fauna (e.g., closeups of species for identification or more panoramic image of the epifauna distribution).
- 39. Describe the statistical parameters that will be used to identify the community parameters (e.g., Shannon-Weaver indicies).

ATTACHMENT II

DETERMINATION OF TOTAL ORGANIC CARBON IN SEDIMENT

July 27, 1988

PREPARED BY: Lloyd Kahn, Quality Assurance Specialist

AFFILIATION: U.S. Environmental Protection Agency, Region II

Environmental Services Division Monitoring Management Branch Edison, New Jersey 08837

1. Score and Application

- <u>.</u> سو This merhod describes protocols for the determination of organic carbon in ocean sediments.
- ; ; Although the detection limit may vary with procedure or a minimum reporting value of 100 mg/kg will be required ocean dumping/dredging program. for the
- 1 Several types of determinations, which are considered equivalent are presented.
- 1.4 Data are reported in mg/kg on a dry weight basis.
- Wet combustion methods are not considered to be equivalent to the pyrolytic methods herein described.

Summer of Method

- 2.1 Inorganic carbon from carbonates and bicarbonates is removed by acid treatment.
- The organic compounds are decomposed by pyrolysis in the presence of oxygen or air.
- 2.3 conductivity gas chromatography, differential thermal conductivity detection by sequential removal of water and carbon distide; or The carbon dioxide that is formed is determined by direct nonthermal conductivity detection following removal of water with magnesium perchlorate. dispersive infrared detection, flame ionization gas chromatography after catalytic conversion of the carbon dioxide to methane; thermal
- 2.4 Water content is determined on a separate portion of sediment

3. Sample Bandling and Preservation

Collect sediments in glass jars with Teflon or aluminum foil. and maintain at 4°C. Analyse within 14 days. 8

4. Interferences

- 4.1 Volatile organics in the sediments may be lost in the decarbonation step resulting in a low bias.
- 4.2 Bacterial decomposition and volatilization of the organic compounds are minimized by maintaining the sample at 4°C, analyzing within the specified bolding time, and analyzing the wat sample.

5. Apparatus

- 5.1 Drying over maintained at 103° to 105°C.
- 5.2 Analytical instrument options:
- 5.2.1 Perkin Blaer Model 2400 Elemental Analyzer or equivalent.

2.

- 5.2.1 I In this instrument, the sample from Section 7.2 is pyrolysed under pure oxygen, water is removed by magnesium perchlorate and the carbon dioxide is removed by ascarite. The decrease in signal obtained by differential thermal conductivity detectors placed between the combustion gas stream before and after the ascarite tube is a measure of the organic carbon content.
- 5.2.2 Carlo Erba Model 1106 CZR Analyser, or equivalent.
- 5.2.2.1 In this apparatus, the sample is pyrolysed in a induction type furnace, and the resultant carbon dioxide is chromatographically separated and analysed by a differential thermal conductivity detector.
- 5.2.3 LZCO Models WR12, WR112, or C2-12 carbon determinators, or Models 600 or 800 CEX analyzers.
- 5.2.3.1 In the LICO WR-12, the sample is burned in high frequency induction furnace, the carbon dioxide is selectively adsorbed at room temperature in a molecular sieve. It is subsequently released by heating and is measured by a thermal conductivity detector. The WR-112 is an upgraded WR-12 employing microprocessor electronics and a printer to replace the electronic digital voltmeter.
- 5.2.3.2 In the LZCC CZ-12 carbon determinator, the sample is combusted in oxygen, moisture and dust are removed by appropriate traps and the carbon dicride is measured by a selective, solid state, infrared detector. The signal from the detector is then processed by a microprocessor and the carbon content is displayed on a digital readout and recorded on an integral printer.
- 5.2.3.3 In the LECO CEN-600 and CEN-800 elemental analyzers, the sample is burned under oxygen in a resistance furnace and the carbon dioxide is measured by a selective infrared detector.
- 5.2.4 Dohrman Model DC35 Digital Righ Temperature TOC Analyser.
- 5.2.4.1 In this instrument, the sample is burned in resistance furnace under oxygen, the interfering gases are removed by a sparger/scrabber system and the carbon dioxide is measured by a non-dispersive infrared detector and shown on a digital display in concentration units.

- 5.3 No specific analyser is recommended as superior. The above listing is for information only and is not intended to restrict the use of other unlisted instruments capable of analyzing TOC. The instruments to be used must have the following specifications:
- 5.3.1 A combustion bost which is heated in a stram of oxygen or air in a resistance or induction-type furnace to completely convert organic substances to CO₂ and water.
- 5.3.2 A means to physically or by measurement technique to separate water and other interferants from CO₂.
- 5.3.3 A means to quantitatively determine ∞_2 with adequate sensitivity (100 mg/kg), and precision (25% at the 95% confidence level as demonstrated by repetitive measurements of a well mixed ocean sediment sample).
- 5.4 A strip thant or other persanent recording device to document the analysis.

6. Leagents

- 6.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank.
- 6.2 Potassium hydrogen phthalata, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml.
 - NOTE 2: Sodium oxalate and acetic acid are not recommended as stock Solutions.
- 6.1 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.
- 6.4 Phosphoric scid solution, 1:1 by volume.

7. Procedure

- 7.1 Weigh the well mixed sample (up to 500 mg) into the combustion boat or cup. Add 1:1 phosphoric acid drop wise until effervescence stops. Heat to 75°C.
 - BOIL: This procedure will convert inorganic carbonates and bicarbonates to carbon dioxide and eliminate it from the easple.
- 7.2 Analyse the residue according to the instrument memufacturer's instructions.

- 7.3 Determine percent res on a separate sample allquot amfollows
 - 7.3.1 Rest a clear 25 ml beaker at 103° to 105°C for one hour. Cool in desicuator, weign to the nearest mg and store in desicuator until use.
- 7.3.2 Add 1 g, weighed to the nearest mg, of an aliquot of the well-mixed sample.
- 7.3.3 Dry and heat in the 103° to 105°C oven for one hour. Cool in desicustor. Weigh to the nearest Eq.

8. Calibration

- 8.1 Follow instrument manufacturer's instructions.
- 8.2 Prepare calibration curve plotting mg carbon vs. instrument response. using four standards and a blank covering the analytical range of interest.

9. Precision and Accuracy

- 9.1 The precision and accuracy will differ with the various instruments and matrices and must be determined by the laboratories reporting data. To initiate a control chart, a representative sample of well mixed sediment should be analyzed 15 times to determine the analytical precision. Set up a control chart showing 3 times the standard deviation limits for precision.
- '9.2 Subsequently during analysis of environmental samples, take one sample per batch of 20 or less and run in quadruplicate. Calculate standard deviation and report with initial control chart data.
- 9.3 If the sample being run in quadruplicate exceeds the 3 standard deviation limit, identify error and rerun environmental samples in that batch along with the quadruplicate sample.